

The physicochemical properties and catalytic performance of molybdate for reduction of H₂O

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Abstract— Hydrogen is an universal energy which can be cleanly produced from water and sunlight on semiconductor oxides. Unlike primary energy sources, hydrogen must be manufactured before storage and used. MoO₃ has received a considerable attention over the last years because of its applications in various fields and mainly in catalysis. The catalyst α -MoO₃ was synthesized by calcination of ammonium heptamolybdate at 700 °C for 6 h, was photo-electrochemically characterized to assess its feasibility for hydrogen production under visible light, an energetic topic. The morphology was analyzed by scanning electronic microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR). The X-ray diffraction (XRD) showed that the MoO₃ powder treated at 700 °C crystallizes in an orthorhombic structure and exhibits a direct optical transition at 2.90 eV. The Mott-Schottky characteristic plotted in (Na₂SO₄, 0.1 M) solution indicates n type conduction with a flat band potential of 0.61 V_{SCE}. As application, hydrogen evolution is successfully realized under visible light; the best performance occurs on MoO₃ at pH ~ 7.

Keywords— MoO₃; semi-conductor; photo-electrochemical; hydrogen; calcinations.

I. INTRODUCTION

Hydrogen is a promising energetic vector because of its clean status; it is used in fuel cells, transport and industrial sector. However, hydrogen differs from other primary energetic sources in that it must be manufactured before its utilization because it is difficult storage or liquefy action. Its in-situ production is necessary and seems to be an attractive solution and remains difficult to put into practice. However, in view of its importance, both scientific and technological advances are being made, as it has become essential to control new technologies producing renewable and sustainable energy. Hydrogen is produced by various methods such as water electrolysis [1-3], coal gasification and reforming methane (steam reforming [4] and dry reforming [5]).

Molybdenum oxides play an important part in industrial applications due to their structural and electronic surface properties. These oxides can act as catalysts in many reactions with the participation of hydrogen or oxygen and can also be used as optical electrochromic materials. MoO₃ is a wide band gap (~3.1 eV) n-type semiconductor, whose conductivity is attributed to oxygen vacancies.

The aim of the present work is focused on the preparation of α -MoO₃ and its application for the photochemical

hydrogen evolution upon visible light. α -MoO₃ is characterized by X-ray diffraction (XRD), Fourier transform infrared (FTIR), chemical analysis, diffuse reflectance spectra, scanning electronic microscopy (SEM) and photoelectrochemistry.

II. EXPERIMENTAL

MoO₃ was synthesized by calcination from (NH₄)₆Mo₇O₂₄·4H₂O at 700°C for 6 h.

The solide was identified by X-ray diffraction (XRD) using INEL XRG 3000 diffractometer with Cu K α anticathode (λ = 0.15405 nm). The morphology was analyzed by scanning electronic microscopy (SEM) taken with microscope PHILIPS XL30-FEG. The Fourier transform infrared (FTIR) spectra were recorded with a FTIR ALPHA Bruker spectrometer. The diffuse reflectance spectrum of MoO₃ was plotted with a Specord 200 Plus spectrophotometer. The Na₂SO₄ solution (0.1M) was deaerated before and during the electrochemical test. The intensity potential J (V) characteristics were plotted with a PGZ301 potentiostat (Radiometer analytical). The capacitance measurements were performed at a frequency of 10 kHz.

The photocatalysis was performed in a Pyrex reactor equipped with a cooling system; the temperature was regulated at 50 ± 1 °C. Three tungsten lamps (200 W) were used for the illumination. The hydrogen was quantified volumetrically by water displacement caused by the pressure developed in the reactor.

III. RESULTS AND DISCUSSION

1- Characterization

The synthesized phases are indexed according to the JCPDS Card N° 47-1320 which confirms the formation of α -MoO₃ crystallizing in the orthorhombic system after treatment at 700 °C, is α -MoO₃ (Fig 1).

The solid MoO₃ (Fig. 2) has a fairly homogeneous structure and a stick-like appearance [6].

The FTIR spectroscopy (Fig. 3) shows characteristic bands of α MoO₃. The vibration bands in the region (800 - 1000 cm⁻¹) are attributed to Mo-O or Mo-O-Mo bonds while the bands (350 - 500 cm⁻¹) are assigned to O-Mo-O [7].

The optical curve (Fig. 4) indicates for MoO₃ an indirect transition 2.90 eV, in agreement with its yellow color. The

capacitance plot (Fig. 5) gives a flat band potential V_{bp} of 0.61 V where the majority charge carriers are electrons, indicating n type behavior.

The potential is negative enough to trigger the H_2 evolution.

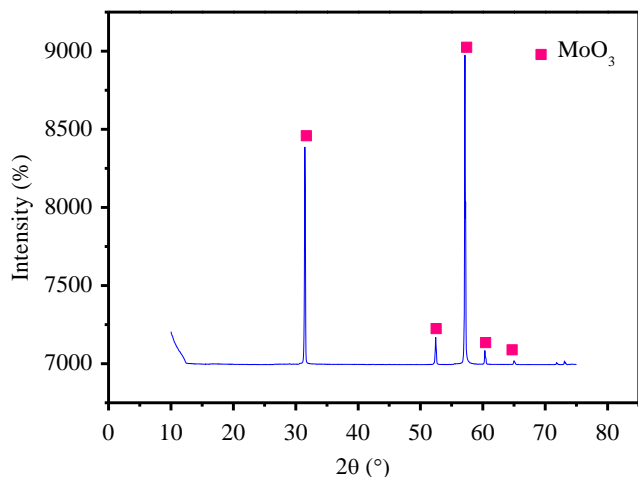


Fig. 1. X-ray diffraction spectrum of MoO_3 .

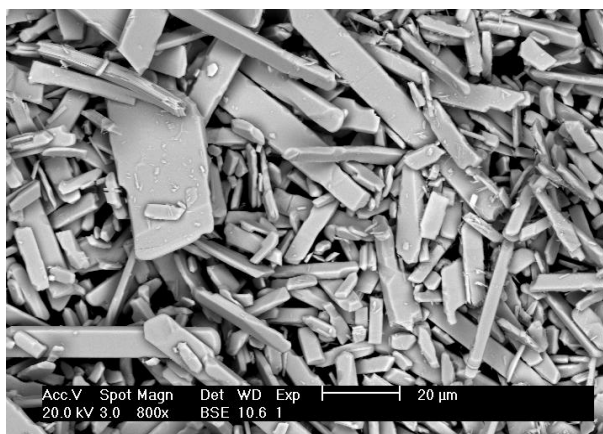


Fig. 2. Micrograph of the solid of MoO_3 .

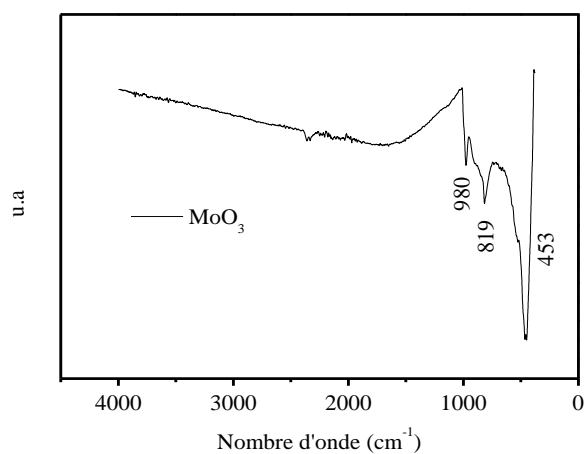


Fig. 3. Analysis FTIR of oxides MoO_3 .

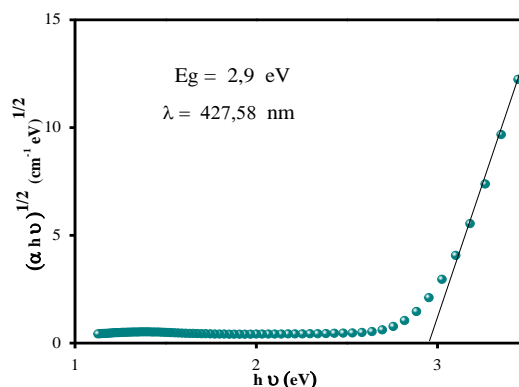


Fig. 4. Indirect optical transition of MoO_3 .

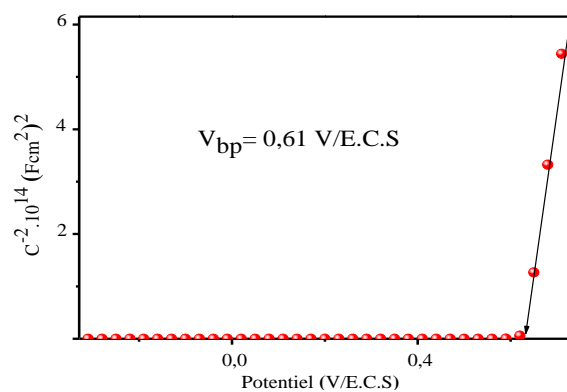


Fig. 5. Measurement of capacitances according to the potential of MoO_3 .

2-Application

The synthesized oxides were successfully applied for the H_2 production under visible light.

2-1- Variation of catalyst mass:

Operating conditions

A masse between 50 and 300 mg of solids MoO_3 + 0.001 M of $Na_2S_2O_3$ in a neutral solution (0.1 M Na_2SO_4), dispersed under magnetic stirring 200 rpm at temperature 50 ± 0.5 °C. The curves of hydrogen production for MoO_3 as a function of the catalyst mass under visible light have the nearly same shape, with a maximum of 200 mg ($MoO_3 = 5.9$ mL) (Fig. 6). The enhanced photoactivity of MoO_3 under visible illumination is partially attributed to the defect states (sub band-gap states) introduced within the gap region during the mechanical treatment on the catalyst surface.

2-2-Variation of pH:

Operating conditions

200 mg of MoO_3 for three different pHs (neutral 0.1 M Na_2SO_4 pH ~ 7 basic pH ~10 and pH = 12) + 0.001 M of $Na_2S_2O_3$, under agitation 200 rpm and at 50 ± 0.5 °C.

Fig 7 shows the results of the photo production of hydrogen against pH. We note that the H₂ production decreases with increasing pH. The best performance is obtained on MoO₃ at pH ~ 7 while no production is observed at pH ~ 12. The performance of MoO₃ is close to that reported by some of us on the delafossite with a similar band gap under the same experimental conditions [8].

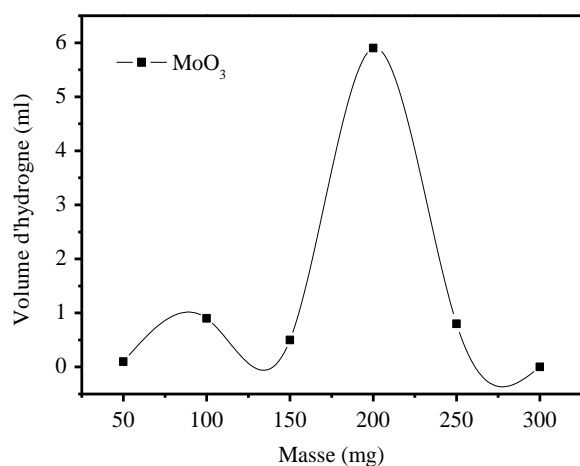


Fig. 6. Evaluation of the quantity of hydrogen produced in presence of MoO₃ as a function of the mass.

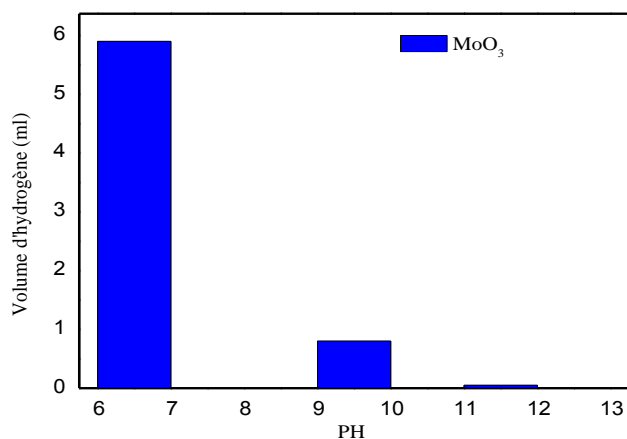


Fig. 7. Evaluation of the quantity of hydrogen produced in the presence of MoO₃ as a function of pH.

CONCLUSION

The operating conditions were optimized to improve the photo production of hydrogen on MoO₃ based compounds prepared by calcination:
A mass of 200 mg of MoO₃ calcined at 700 °C in a neutral medium (0.1 M Na₂SO₄).

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